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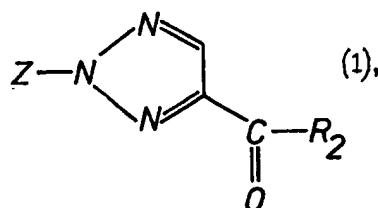
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(54) Novel 2-phenyl-2H-1,2,3-triazoles and their use in the preparation of fluorescent whitening agents series.

(57) Novel 2-phenyl-2H-1,2,3-triazoles of the formula



wherein R₂ is C₁-C₆ alkyl, unsubstituted or substituted phenyl or benzyl and Z is unsubstituted or substituted phenyl, are useful intermediates for obtaining fluorescent whitening agents of the 3-(2'-phenyl-2'H-1',2',3'-triazol-4'-yl)coumarin

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SPECIFICATION

2-Phenyl-2H-1,2,3-triazoles, processes for the preparation thereof and use thereof

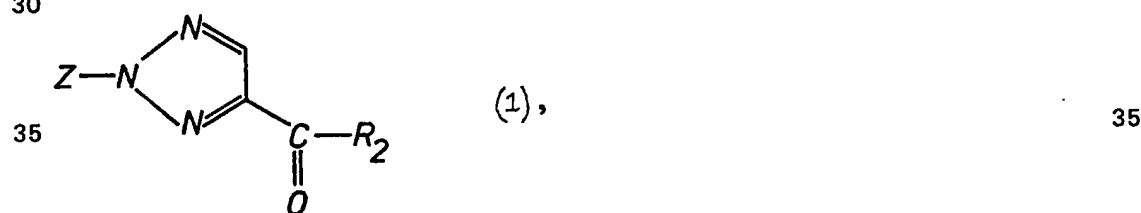
5 The present invention relates to novel 2-phenyl-4-alkanoyl-(or -benzoyl)-2H-1,2,3-triazoles, to processes for the preparation thereof, and to the use thereof for the production of 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids and derivatives thereof which are used as starting materials for obtaining fluorescent whitening agents of the 3-(2'-phenyl-2'H-1',2',3'-triazol-4'-yl)coumarin series. The invention relates further to a process for the preparation of said triazolylacetic acids, and to novel intermediates which are obtained in the course of the preparation of the 2-phenyl-4-alkanoyl- (or -benzoyl)-2H-1,2,3-triazoles of this invention.

2-Phenyltriazoles and processes for obtaining them are known. In this connection, attention is drawn to the following literature incorporated herein by way of reference: the articles by F.R. Benson et al. in Chem. Rev. 46, 1 (1950) and by T.L. Gilchrist et al. in Adv. in Heterocyclic Chem. 16, 33 (1974), Academic Press, New York and London; Chem. Abstr. Vol. 79 (1973), 66367n, Swiss patent 485 014, German Auslegeschrift 1 168 437, German patent 1 226 591, E. Klingsberg, Synthesis 1972 (9) 475-7, and Chem. Ber. 98(4), 1335-41 (1965) (= Chem. Abstr. Vol. 62 (1965), 16090d).

It is an object of the present invention to provide novel specifically substituted 2-phenyl-2H-1,2,3-triazoles which are particularly useful intermediates for obtaining fluorescent whitening agents. It is a further object of the invention to find a novel method of synthesising 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids and their derivatives, which are of great importance for obtaining fluorescent whitening agents of the 3-(2'-phenyl-2'H-1',2',3'-triazol-4'-yl)coumarin series.

25 Surprisingly, it has now been found that the novel 2-phenyl-4-alkanoyl- (or -benzoyl)-2H-1,2,3-triazoles of the present invention meet these requirements. A number of novel intermediates which are obtained in the course of the preparation of these useful compounds likewise constitute an object of the invention.

The 2-phenyl-2H-1,2,3-triazoles of the present invention have the formula



40 wherein R₂ is C₁-C₈ alkyl, unsubstituted or substituted phenyl or benzyl, and Z is unsubstituted or substituted phenyl.

Examples of possible substituents for the phenyl ring Z or for R₂ as phenyl or benzyl are: halogen, alkyl, alkoxy, nitro, cyano, trifluoromethyl, alkenyl, cycloalkyl, substituted alkyl or alkoxy such as alkoxyalkyl, alkoxyalkoxy, hydroxyalkyl, hydroxyalkoxy, haloalkyl, haloalkoxy, cyanoalkyl, carboxyalkyl, sulfoalkyl, phenylalkyl, phenoxyalkyl or carbalkoxyalkyl, carboxyl and sulfo and their derivatives, phenylsulfonyl, or phenyl or phenoxy, each of which may be mono- or polysubstituted (e.g. disubstituted) by halogen, alkyl, alkoxy, carbalkoxy, alkylsulfonyl, cyano, nitro, trifluoromethyl, carboxyl or sulfo and their derivatives; and also groups of the formulae



NY¹Y², -S(O)_n alkyl or -S(O)_n-(substituted alkyl), where substituted alkyl groups may be those specified above, n is 0, 1 or 2, and each of Y¹ and Y² independently of the other is hydrogen, alkyl, substituted alkyl as defined above, or Y¹ and Y² together with the nitrogen atom to which they are attached form a 5- or 6-membered saturated heterocyclic ring which may additionally contain 1 or 2 nitrogen, oxygen and/or sulfur atoms as ring members and may be substituted by alkyl groups.

60 Substituted phenyl or benzyl groups R₂ can contain two of the substituents listed above, but it is preferred that they contain one substituent. The number of such substituents contained by the phenyl radical Z is in particular three, preferably two or one. The number of second order substituents or sterically hindering radicals present in the phenyl nucleus is preferably at most two and most preferably only one.

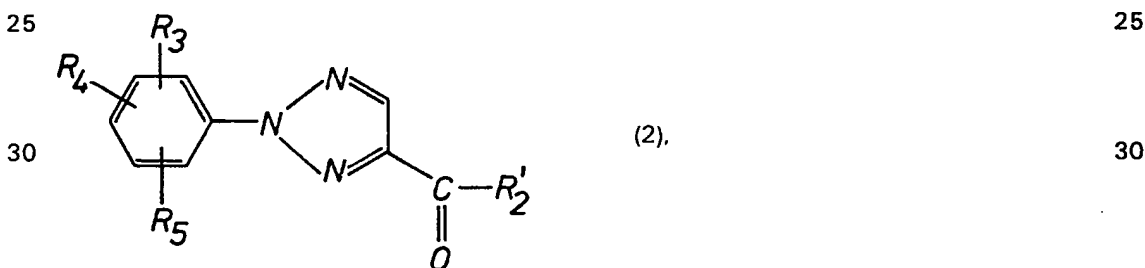
65 Halogen is chlorine, fluorine or bromine, with chlorine being preferred. Alkyl and alkoxy

groups may contain 1 to 8, e.g. 1 to 6, preferably 1 to 4, carbon atoms. This also applies in respect of alkyl or alkoxy moieties in complex radicals (e.g. alkoxyalkyl, alkoxyalkoxy, carbalkoxy etc.) and also of substituted alkyl or alkoxy groups. Alkenyl preferably contains 2 to 6, most preferably 3 or 4, carbon atoms.

- 5 Derivatives of sulfo or carboxyl groups are preferably salts, esters and amides. The amides may have the formula $-\text{SO}_2\text{NY}^1\text{Y}^2$ or CONY^1Y^2 , in which Y^1 and Y^2 are as defined above. Provided they contain additional hetero-atoms in the ring, saturated nitrogen-containing heterocyclic rings $\text{Y}^1 + \text{Y}^2$ preferably contain a nitrogen, oxygen and/or sulfur atom as such additional hetero-atoms. Possible alkyl substituents preferably contain 1 to 4 carbon atoms. Examples of
10 such nitrogen-containing heterocyclic rings are the piperidine, piperazine, imidazolidine, pyrrolidine, morpholine, thiomorpholine or oxazolidine ring.

- Salts of carboxyl and sulfo groups (throughout this specification, "carboxyl" and "sulfo" will always be understood as also meaning their salts) may be in particular alkali metal, alkaline earth metal, ammonium or amine salt ions. The sulfo and carboxyl groups will then have the
15 formula $-\text{COOM}$ and $-\text{SO}_3\text{M}$ respectively, wherein M is hydrogen or a salt-forming cation. A suitable salt-forming cation is e.g. an alkali metal, ammonium or amine salt ion. Preferred amine salt ions are those of the formula $\text{H}^+\text{NR}_1^i\text{R}_2^i\text{R}_3^i$, in which R_1^i , R_2^i and R_3^i independently of one another are hydrogen, alkyl, alkenyl, hydroxyalkyl, cyanoalkyl, haloalkyl or phenylalkyl, or in which R_1^i and R_2^i together complete a 5- or 6-membered saturated nitrogen-containing heterocyclic ring which may additionally contain a nitrogen or oxygen atom as ring member, for example
20 a piperidine, piperazine, pyrrolidine, imidazolidine or morpholine ring, and R_3^i is hydrogen.

Interesting compounds within the scope of formula (1) are the 2-phenyl-2H-1,2,3-triazoles of the formula



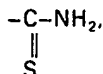
- 35 wherein R_2' is C_1 - C_6 alkyl, unsubstituted phenyl or benzyl, or phenyl or benzyl substituted by one or two members selected from the group consisting of halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_3 - C_4 alkenyl, nitro, cyano, carboxyl or sulfo and their derivatives, C_2 - C_6 carbalkoxy or trifluoromethyl; and R_3 , R_4 and R_5 independently of one another are hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_3 - C_4 alkenyl, C_1 - C_4 -alkoxy, C_1 - C_4 haloalkoxy, C_2 - C_6 alkoxyalkoxy, or phenyl or phenoxy which is unsubstituted or mono- or polysubstituted by halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_6 carbalkoxy, C_1 - C_4 -alkylsulfonyl, cyano, nitro, trifluoromethyl or a group of the formula $-\text{COOY}_3$ or $-\text{SO}_3\text{Y}_3$; or are a group of the formula
40



- 50 $-\text{NY}_1\text{Y}_2$, $-\text{SO}_3\text{Y}_3$, $-\text{COOY}_3$, $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{alkyl})$ or $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{haloalkyl})$, wherein each of Y_1 and Y_2 independently of the other is hydrogen or C_1 - C_6 alkyl, Y_3 is hydrogen, C_1 - C_4 alkyl or a salt-forming cation and n is 0, 1, or 2.

Where R_2 is a substituted phenyl or benzyl radical, it preferably contains one of the indicated substituents.

- 55 In formula (2), the substituents R_3 , R_4 and R_5 have the following preferred meanings:
 R_3 : hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_3 - C_4 alkenyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_2 - C_6 alkoxyalkoxy, phenyl or phenoxy which is unsubstituted or mono- or polysubstituted by halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_6 carbalkoxy, C_1 - C_4 alkylsulfonyl, cyano, nitro, trifluoromethyl or a group of the
60 formula $-\text{COOY}_3$ or $-\text{SO}_3\text{Y}_3$; or a group of the formula



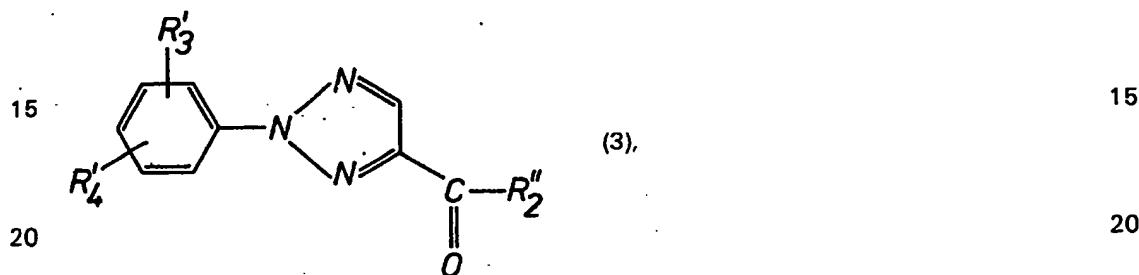
$-\text{NY}_1\text{Y}_2$, $-\text{SO}_3\text{Y}_3$, $-\text{COOY}_3$, $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{alkyl})$ or $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{haloalkyl})$, wherein each of Y_1 and Y_2 independently of the other is hydrogen or $\text{C}_1-\text{C}_8\text{alkyl}$, Y_3 is hydrogen, $\text{C}_1-\text{C}_8\text{alkyl}$ or a salt-forming cation and n is 0, 1 or 2;

R_4 : hydrogen, halogen, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, nitro, cyano, $\text{C}_1-\text{C}_4\text{haloalkyl}$, $-\text{NY}_1\text{Y}_2$, $-\text{SO}_3\text{Y}_3$, $-\text{COOY}_3$ or $\text{C}_1-\text{C}_4\text{alkylsulfonyl}$; 5

R_5 : hydrogen, halogen, $\text{C}_1-\text{C}_4\text{alkyl}$ or $\text{C}_1-\text{C}_4\text{alkoxy}$.

Suitable salt-forming cations Y_3 are preferably those specified above for M^\oplus . Alkali metal ions and ammonium ions are preferred. Preferred derivatives of sulfo and carboxyl groups are likewise those exemplified at the outset under formula (1).

10 Particularly interesting compounds are the 2-phenyl-1,2,3-triazoles of the formula 10

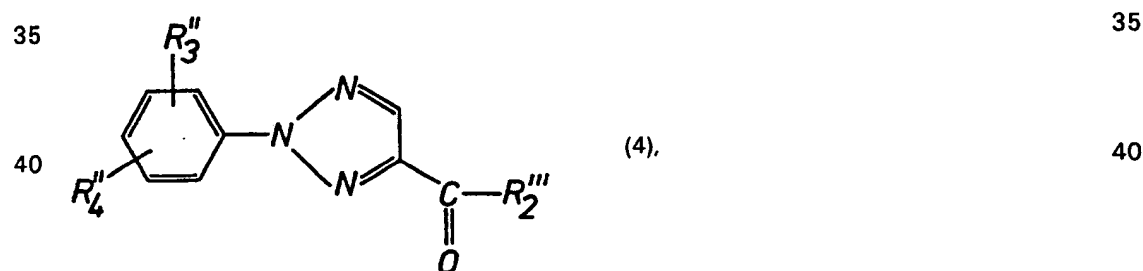


wherein R_2'' is C_1-C_4 alkyl, benzyl, phenyl or phenyl which is substituted by one or two members selected from the group consisting of chlorine, C_1-C_4 alkyl, methoxy, nitro, cyano and/or trifluoromethyl, and each of R_3' and R_4' independently of the other is hydrogen, halogen, trifluoromethyl, cyano, nitro, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, $\text{C}_1-\text{C}_4\text{alkylsulfonyl}$, or phenyl or phenoxy which is unsubstituted or substituted by halogen, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, cyano, nitro, trifluoromethyl or a group of the formula $-\text{COOY}_3'$ or $-\text{SO}_3\text{Y}_3'$; or is a group of the formula $-\text{SO}_3\text{Y}_3$, $-\text{COOY}_3$ or $-\text{NY}_1\text{Y}_2$, wherein Y_1 , Y_2 and Y_3 are as defined for formula (2) and Y_3' is 25

hydrogen, an alkali metal ion or an ammonium ion. 30

R_4' in formula (3) is preferably hydrogen, halogen, cyano, nitro, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, $\text{C}_1-\text{C}_4\text{alkylsulfonyl}$, $-\text{COOY}_3$, $-\text{SO}_3\text{Y}_3$ or $-\text{NY}_1\text{Y}_2$.

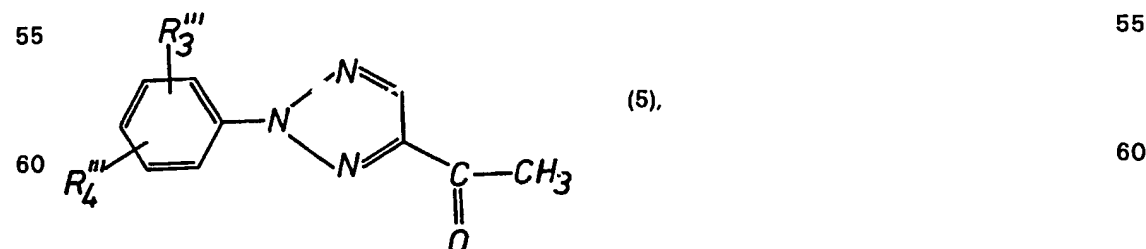
Useful compounds are in particular the 2-phenyl-2H-1,2,3-triazols of the formula



45 wherein R_2''' is $\text{C}_1-\text{C}_4\text{alkyl}$, benzyl, phenyl or phenyl which is substituted by one or two members selected from the group consisting of chlorine, methoxy and/or methyl, R_3'' is hydrogen, halogen, trifluoromethyl, cyano, nitro, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, $\text{C}_1-\text{C}_4\text{alkylsulfonyl}$, phenyl or phenoxy which is unsubstituted or substituted by chlorine, methyl, methoxy, cyano, 50

nitro, sulfo or carboxyl or the alkali metal salts or ammonium salts thereof; or is a group of the formula $-\text{SO}_3\text{Y}_3'$, $-\text{COOY}_3'$ or $-\text{NY}_1\text{Y}_2$, wherein Y_1 , Y_2 and Y_3' are as defined for formula (3); and R_4'' is hydrogen, halogen, $\text{C}_1-\text{C}_4\text{alkyl}$ or $\text{C}_1-\text{C}_4\text{alkoxy}$.

Preferred 2-phenyl-2H-1,2,3-triazoles have the formula



wherein R_3'' is hydrogen, halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, cyano, nitro, sulfo or carboxyl and the alkali metal salts or ammonium salts thereof, C_1 - C_4 alkylsulfonyl, phenoxy, phenyl, chlorophenyl, methylphenyl or carboxyphenyl and the alkali metal salts or ammonium salts thereof, and R_4'' is hydrogen, halogen, methyl or methoxy.

5 Particularly preferred compounds are also those of the formulae (1) to (4), wherein R_2 , R_2' , R_2'' and R_2''' are methyl. 5

The processes described below for the preparation of compounds of the formulae (1) to (5) also constitute an object of the invention.

A first process for the preparation of compounds of the formula (1), and thus also of the 10 subformulae (2) to (5), comprises cyclising an oxime of the formula 10



wherein Z and R_2 are as defined for formula (1), in the presence of a condensing agent, to give the corresponding triazole.

20 The compounds of formulae (2) to (5) are prepared in analogous manner by using starting materials of the formula (6), in which R_2 and the phenyl radical Z are as defined for formulae (2) to (5). The preferred starting material is an oxime of the formula (6), wherein R_2 is methyl. 20

As condensing agent in the process of this invention it is preferred to use an acid anhydride or an acid halide, for example acetic anhydride, propionic anhydride, acetyl chloride, benzoyl chloride, benzene sulfochloride, toluene sulfochloride, methane sulfochloride, ethane sulfochloride, phosphoroxy chloride or thionyl chloride. The preferred condensing agent is acetic anhydride. 25

The process of the invention yields the best results (high yields, pure products) if it is carried out in aqueous medium with acetic anhydride as condensing agent. The pH is kept between 10 and 13, preferably between 11 and 12, during the cyclisation. The reaction temperature can be 30 in the range from 0° to 100°C, but is preferably from 0° to 50°C and, most preferably, from 5° to 25°C. 30

In the above described preferred variant of the process of this invention, the reaction medium consists of acetic anhydride and water. However, a water-miscible organic solvent may 35 additionally be present in the reaction medium. Instead of the water-miscible solvent, a water-immiscible organic solvent may also be used. This variant can be especially advantageous if a water-insoluble compound of the formula (1) is obtained. The final product then dissolves in the organic phase and with the organic phase is separated from the reaction mixture and worked up. 35

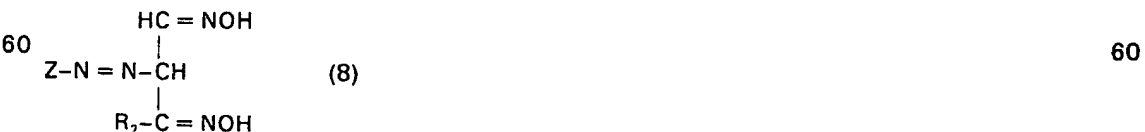
40 Examples of suitable water-miscible organic solvents are lower aliphatic alcohols such as methanol, ethanol, isopropanol, n-propanol, butanol and ethylene glycol, ethyl glycol monoalkyl ethers, tetrahydrofuran, dioxan, formamide, dimethyl formamide, and similar solvents. 40

Examples of water-immiscible solvents which may be used are: liquid aliphatic hydrocarbons and mixtures thereof, halogenated, preferably chlorinated, aliphatic hydrocarbons, e.g. methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, etc., aromatic hydrocarbons such as benzene, toluene, xylene, chlorinated aromatic hydrocarbons such as chlorobenzene, dichlorobenzene or trichlorobenzene, and similar solvents. 45

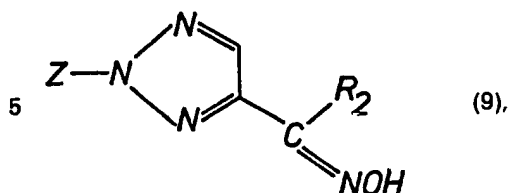
A further process for obtaining 2-phenyl-2H-1,2,3-triazoles of the formula (1) and of the subformulae (2) to (5), comprises reacting a compound of the formula 50



with hydroxylamine or a salt thereof, to give a dioxime of the formula



65 cyclising this dioxime, in the presence of a condensing agent, to give a triazole of the formula 65



and hydrolysing this product to the corresponding ketone. In the formulae (7) to (9) above, the general symbols have the meanings given for formula (1). The compounds of formulae (2) to (5) are obtained in similar manner, by using starting compounds of the formula (7), in which R_2 and the phenyl radical Z are as defined in formulae (2) to (5). Preferred starting compounds are those of the formula (7) in which R_2 is methyl.

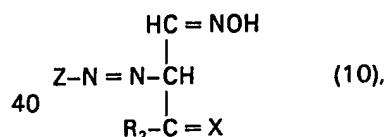
The reaction of a compound of the formula (7) with hydroxylamine or a salt thereof (first step) is conveniently carried out in an inert solvent, preferably in pyridine. The reaction temperature can be in the range from 0° to 50°C , preferably from 5° to 25°C .

The dioxime of the formula (8) is cyclised in the presence of a condensing agent to give the triazole of the formula (9). This second step may be carried out in exactly the same manner as the cyclisation of a compound of the formula (6) described above. The preferred condensing agents, reaction medium, pH value, reaction temperatures and solvents for this second step of the second process of the invention are exactly the same as those specified above for the cyclisation of the compound of formula (6), so that a repetition of these particulars may be dispensed with.

The hydrolysis of the triazoles of formula (9) obtained after the second step may be carried out in conventional manner in acid or alkaline medium (third step). It is preferred to carry out the hydrolysis in the presence of sodium bisulfite or of formaldehyde or paraformaldehyde. In particular, it is carried out in water or a mixture of water and a water-miscible organic solvent (e.g. one of those listed above), preferably a lower aliphatic alcohol, and preferably at elevated temperature, especially at the boiling point of the reaction medium.

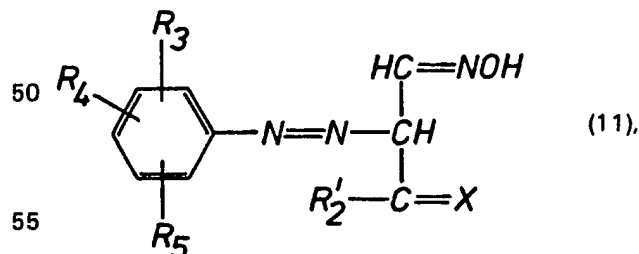
The intermediates of the formulae (6) and (8) obtained in the two processes just described for the preparation of the triazoles of the formula (1) are novel and also constitute an object of the present invention.

In another of its aspects the present invention accordingly relates to the oximes of the formula



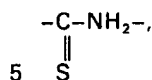
wherein R_2 is C_1 - C_6 alkyl, unsubstituted or substituted phenyl or benzyl, Z is unsubstituted or substituted phenyl and X is O or NOH.

Particularly interesting oximes are those of the formula



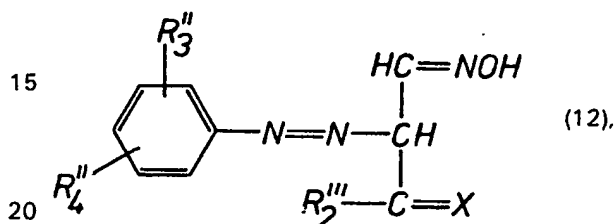
wherein X is O or NOH, R_2' is C_1 - C_6 alkyl, unsubstituted phenyl or benzyl or phenyl or benzyl which is substituted by one or two members selected from the group consisting of halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_3 - C_4 alkenyl, nitro, cyano, or carboxyl or sulfo and derivatives thereof, C_2 - C_6 carbalkoxy or trifluoromethyl, and R_3 , R_4 and R_5 independently of one another are hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_3 - C_4 alkenyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_2 - C_6 alkoxyalkoxy, unsubstituted phenyl or phenoxy or phenyl or phenoxy which is mono- or polysubstituted by halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_6 carbalkoxy, C_1 - C_4 alkylsulfonyl, cyano, nitro, trifluoromethyl or a

group of the formula $-\text{COOY}_3$ or $-\text{SO}_3\text{Y}_3$; or are a group of the formula



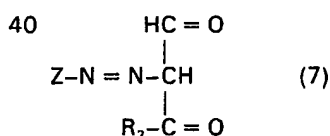
$-\text{NY}_1\text{Y}_2$, $-\text{SO}_3\text{Y}_3$, $-\text{COOY}_3$, $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{alkyl})$ or $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{haloalkyl})$, wherein each of Y_1 and Y_2 independently of the other is hydrogen or $\text{C}_1-\text{C}_5\text{alkyl}$, Y_3 is hydrogen, $\text{C}_1-\text{C}_5\text{alkyl}$ or a salt-forming cation, and n is 0, 1 or 2. The substituents R_2 , R_3 , R_4 and R_5 are preferably as defined for formula (2).

Preferred oximes are those of the formula



wherein X is O or NOH , R_2''' is $\text{C}_1-\text{C}_4\text{alkyl}$, benzyl, phenyl or phenyl substituted by one or two members selected from the group consisting of chlorine, methoxy and/or methyl, R_3'' is hydrogen, halogen, trifluoromethyl, cyano, nitro, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, $\text{C}_1-\text{C}_4\text{alkylsulfonyl}$, unsubstituted phenyl or phenoxy or phenyl or phenoxy which is substituted by chlorine, methyl, methoxy, cyano, nitro, or sulfo or carboxyl or the alkali metal salts or ammonium salts thereof; or is a group of the formula $-\text{SO}_3\text{Y}_3'$, $-\text{COOY}_3'$ or $-\text{NY}_1\text{Y}_2$, wherein Y_1 , Y_2 and Y_3' are as defined for formula (3); and R_4'' is hydrogen, halogen, $\text{C}_1-\text{C}_4\text{alkyl}$ or $\text{C}_1-\text{C}_4\text{alkoxy}$, with R_3'' preferably being hydrogen, halogen, $\text{C}_1-\text{C}_4\text{alkyl}$, $\text{C}_1-\text{C}_4\text{alkoxy}$, cyano, nitro, sulfo or carboxyl and the alkali metal salts or ammonium salts thereof, $\text{C}_1-\text{C}_4\text{alkylsulfonyl}$, phenoxy, phenyl, chlorophenyl, methylphenyl or carboxyphenyl and the alkali metal salts or ammonium salts thereof, and R_4'' preferably being hydrogen, halogen, methyl or methoxy.

In the formulae (10) to (12) above, R_2 , R_2' and R_2''' are preferably methyl and X is O . The compounds of formulae (10) to (12), in which X is NOH , are obtained as described above for the oximation of a compound of the formula (7). Compounds of formulae (10) to (12), in which X is O , i.e. also compounds of formula (6), can be obtained by reacting a compound of the formula

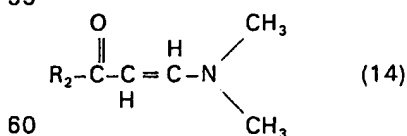


with hydroxylamine or a salt thereof, in a lower alcohol, preferably ethanol, with the addition of sodium acetate, to give the corresponding monooxime of the formula (6) [q.v. also the Examples herein].

The starting compounds of the formula (7) are obtained e.g. by diazotising a corresponding aniline of the formula



and coupling the resultant diazonium salt solution with a compound of the formula

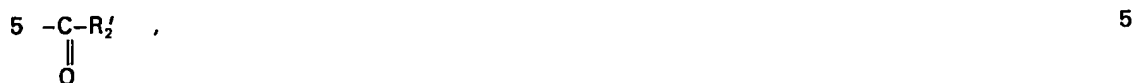


[q.v. D. Leuchs, Chem. Ber. 98, 1335 (1965)]. Reference is also made to the Examples herein.

The compounds of the formula (14) are known or they may be readily obtained by known methods.

The intermediates of the formula (9) obtained in the second process described above for the

preparation of compounds of the formula (1) are novel and also constitute an object of the present invention. Preferred compounds of the formula (9) correspond to those of the formulae (2) to (5), except that the group



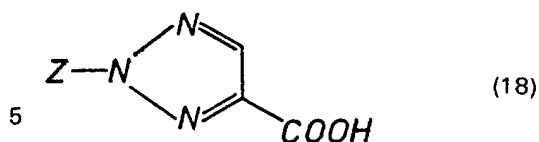
25 is replaced by the group 25



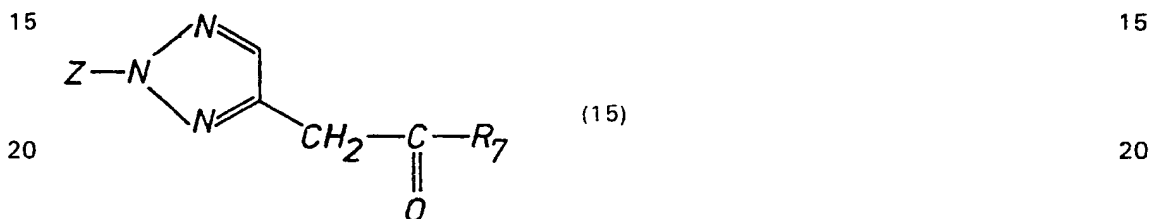
45 Preferred compounds here are also the oximes in which R_2 , R_2' , R_2'' and R_2''' are methyl. 45

The 2-phenyl-2H-1,2,3-triazoles of the formula (1), wherein R_2 is methyl, are valuable intermediates for obtaining 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids and derivatives thereof which, in turn, are intermediates for obtaining fluorescent whitening agents. The use of the novel compounds of the formula (1) provides a novel and especially advantageous method of preparing these important triazolylacetic acids. Up to now these acetic acids have been obtained by different methods, all of which, however, involve certain shortcomings and difficulties. Reference is made in this connection to German Offenlegungsschrift 2 329 991, Netherlands published patent specification 74-07127, Chem. Abstr. 88, 170153n (1978), and Chem. Abstr. 87, 201547 (1977).

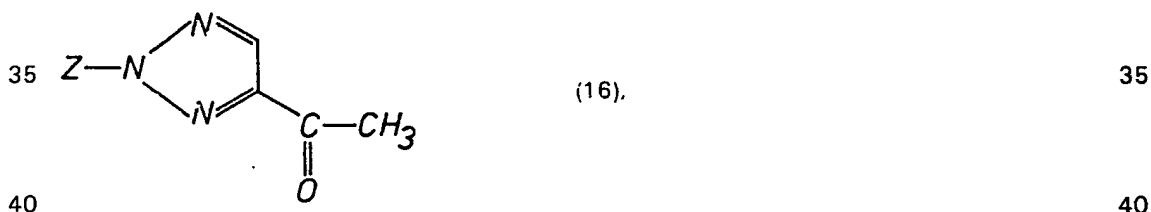
50 The other 2-phenyl-2H-1,2,3-triazoles of the formula (1), wherein R_2 is different from methyl, can also be used as intermediates for obtaining the above mentioned 2-phenyl-2H-1,2,3-triazolyl-4-acetic acids and their derivatives. For this purpose they can first be converted by known methods into compounds of the formula (1), in which R_2 is methyl, and which compounds, as described hereinafter, can be reacted to give the corresponding triazolylacetic acids. For example, triazoles of the formula (1), wherein R_2 is different from methyl, can first be oxidised to an acid of the formula 55 60



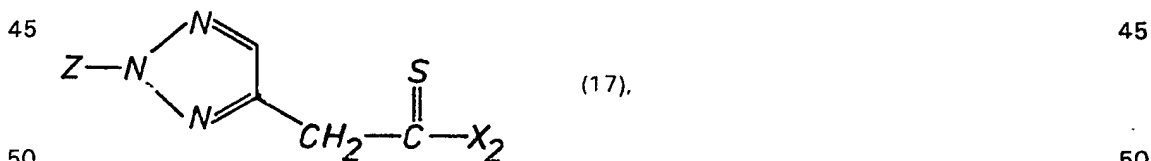
preferably with the aid of KMnO_4 . The acids of the formula (18) can then be converted into the corresponding acid chlorides (e.g. by chlorination with PCl_3 , PCl_5 , SOCl_2 , SO_2Cl_2 etc.), which
 10 chlorides are then reacted with a methyl magnesium halide (CH_3MgX , in which X is Cl, Br or I) 10
 by Grignard reaction to give the corresponding triazoles of the formula (1), wherein R_2 is methyl.
 The above process steps are known per se from textbooks of organic chemistry.
 2-Phenyl-2H-1,2,3-triazol-4-yl-acetic acids of the formula



wherein Z is unsubstituted or substituted phenyl and R_7 is hydroxyl, C_1 - C_4 alkoxy or a group of
 25 the formula $-\text{O}^-\text{M}^+$ or $-\text{NY}_4$, wherein each of Y_4 and Y_5 independently of the other is 25
 hydrogen or C_1 - C_5 alkyl, or Y_4 and Y_5 together with the nitrogen atom to which they are attached
 form a 5- or 6-membered saturated heterocyclic ring which may additionally contain an oxygen,
 sulfur and/or nitrogen atom as ring members and which may be substituted by one or two
 C_1 - C_4 alkyl groups, and M^+ is a salt-forming cation, and the derivatives thereof, may be
 30 prepared in particularly advantageous manner by reacting a 2-phenyl-2H-1,2,3-triazole of the 30
 formula



with morpholine, piperidine or dimethylamine and sulfur, to give a 2-phenyl-2H-1,2,3-triazol-4-yl-thioacetamide of the formula



wherein X_2 is



65 or $-\text{N}(\text{CH}_3)_2$, and hydrolysing this product, without isolating it, to give the corresponding 2- 65

phenyl-2H-1,2,3-triazol-4-yl-acetic acid and, if desired, converting said acid by conventional methods into a salt, an ester or an amide. This process constitutes a further object of the present invention.

Definitions of preferred salt-forming cations M^{\oplus} and of preferred 5- or 6-membered saturated heterocyclic rings ($Y_4 + Y_5$) in formula (15) are stated at the outset in connection with formula (1) [e.g. $Y_1 + Y_2$] and such preferences also apply to compounds of the formula (15).

Preferred triazolylacetic acids of formula (15) are obtained by using compounds of formulae (2) to (5) [in which $R_2 = CH_3$] as starting materials instead of compounds of formula (1). The optional conversions of resultant compounds of the formula (15), wherein R_7 is OH (free acid), into corresponding salts, esters and amides, can be carried out by conventional methods of salt formation, esterification and amidation.

Triazolylacetic acids of the formula (15) are prepared by reacting preferably a compound of the formula (16) with morpholine, piperidine or dimethylamine and powdered sulfur (Willgerodt-Kindler reaction). Amines other than those specified may also be used, e.g. diethylamine, piperazine, thiomorpholine and other amines conventionally employed for the Willgerodt-Kindler reaction. The reaction is ordinarily conducted without a solvent. The reaction temperature is in the range from about 50° to 150°C, preferably from 80° to 120°C. The thioamide obtained, which is usually not isolated, can then be hydrolysed with a base, in aqueous medium, to the corresponding acetic acid or salt thereof. As base it is preferred to use an alkali metal hydroxide, in particular NaOH. The hydrolysis is conveniently carried out at elevated temperature, preferably at reflux temperature.

Alternatively, the conversion of the acetyltriazoles of the formula (16) into the corresponding triazolylacetic acid may be carried out with ammonium polysulfide and by subsequent hydrolysis of the intermediate (Willgerodt reaction). A solvent, e.g. dioxan, may also be used concurrently in this variant.

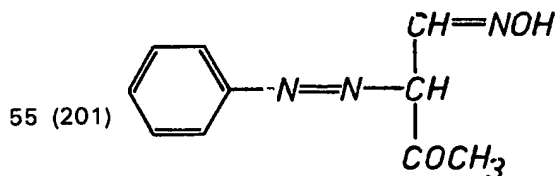
Some of the compounds of formula (15) are known but many are novel. The compounds of the formula (15), where they are novel, likewise constitute an object of the invention.

As already mentioned, the triazolylacetic acids and their derivatives of the formula (15) can be used for obtaining fluorescent whitening agents of the 3-(2'-phenyl-2'H-1',2',3'-triazol-4'-yl)coumarin series. Processes for obtaining such fluorescent whitening agents using 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids and their derivatives are described in US patent specification 3 966 755 and British patent specification 1 412 049.

As already mentioned, 2-phenyl-4-acetyltriazoles which are substituted in the 5-position by a methyl group are also known from the literature. Reference is made in this connection e.g. to German patent specification 1 226 591, E. Klingsberg, *Synthesis* 1972 (9), 475-7 and *Chem. Ber.* 98 (4), 1335-41 (1965). Surprisingly, however, the triazoles of the formula (1) which are unsubstituted in the 5-position are more useful intermediates to the extent that the 3-(2'-phenyl-2'H-1',2',3'-triazol-4'-yl)coumarin fluorescent whitening agents obtainable therefrom (via the intermediate of the corresponding triazolylacetic acids) have substantially more advantageous whiteners properties. Substantially better degrees of whiteness are obtained e.g. on textile materials such as those made from synthetic fibres, especially polyester fibres, than with those fluorescent whitening agents which are obtainable from 2-phenyl-4-acetyl-1,2,3-triazoles, which are substituted in the 5-position by methyl.

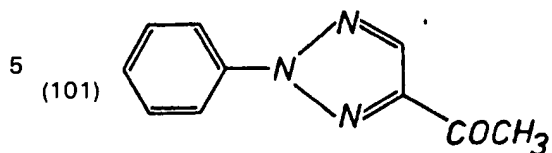
The following Examples illustrate the different aspects of the present invention in more detail without implying any restriction to what is described therein. Parts and percentages are by weight, unless otherwise stated. Melting points and boiling points are uncorrected, unless otherwise indicated.

Example 1: 205 g of 2-phenylazoacetaldehyde-1-oxime of the formula



are dissolved in 1250 ml of water of 40°C which contain 44 g of sodium hydroxide. With stirring, the solution is cooled to 15°C and the sodium salt of the oxime partially precipitates. With efficient stirring, 112 g of acetic anhydride are then added dropwise over the course of 1 hour. The pH is kept between 11.5 and 12 by the simultaneous dropwise addition of concentrated sodium hydroxide solution and the temperature is kept at 15°-17°C by external cooling. The reaction product which has precipitated after completion of the reaction is filtered with suction, washed with water and dried. Yield: 179 g (96% of theory) of 4-acetyl-2-phenyl-

2H-1,2,3-triazole of the formula

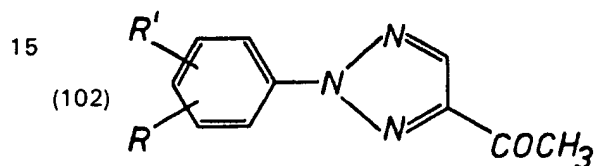


5

10 in the form of a beige-coloured product which melts at 95°–96°C after recrystallisation from hexane.

10

The 4-acetyl-2-phenyl-2H-1,2,3-triazoles of the formula




15

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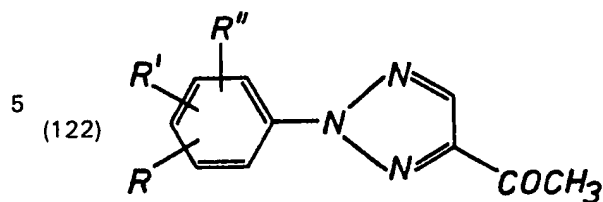
listed in Table 1 are obtained in analogous manner using the correspondingly substituted 2-phenylazoacetoacetaldehyde-1-oximes of the formulae (203)–(221) as starting materials (see Example 2).

20

Table 1

5	Compound	R	R'	melting point (°C)	5
	103	4-CN	H	154-157	
10	104	4-CH ₃	H	82-83	10
	105	3-CH ₃	H	60-61	
	106	2-CH ₃	H	59-60	
15	107	4-Cl	H	110-111	15
	108	3-Cl	H	113-114	
	109	2-Cl	H	70-72	
20	110	4-OCH ₃	H	112-113	20
	111	3-OCH ₃	H	72-73	
25	112	2-OCH ₃	H	58-60	25
	113	4-COOH	H	261-262	
	114	4-NO ₂	H	123-125	
30	115	4-O-C ₆ H ₅	H	108-110	30
	116	4-Cl	2-Cl	103-105	
	117	4-SO ₂ CH ₃	H	176-178	
35	118	3-SO ₃ Na	H	>300	35
40	119	4- 	H	268-269	40
	120	4-F	H	114-118	
45	121	4-Br	H	114-116	45

The 4-acetyl-2-phenyl-2H-1,2,3-triazoles of the formula



10

listed in Table 1a are also obtained in analogous manner by using the correspondingly substituted 2-phenylazoacetaldehyde-1-oximes of the formulae (223)–(273) as starting materials (see Example 2).


10

15 Table 1a.

15

Compound	R	R'	R''
20 123	4-C ₂ H ₅	H	H
124	3-Br	H	H
125	2-F	H	H
25 126	4-I	H	H
127	3-I	H	H
30 128	2-I	H	H
129	4-CF ₃	H	H
130	2-CF ₃	H	H
35 131	4-i-C ₃ H ₇	H	H
132	4-N(CH ₃) ₂	H	H
133	3-CH ₃	4-Br	H
40 134	3-NH ₂	H	H
135	3-NHSO ₂ CF ₃	H	H
136	3-NO ₂	4-CH ₃	H
45 137	3-NH ₂	4-CH ₃	H
138	3-NHSO ₂ CF ₃	4-CH ₃	H
139	3-Cl	4-CH ₃	H
50 140	3-NH ₂	4-Cl	H
141	3-NHSO ₂ CF ₃	4-Cl	H
142	3-Cl	4-Cl	H
55 143	3-OCH ₃	4-OCH ₃	H
144	3-OCH ₃	5-OCH ₃	H
60 145	3-Cl	5-Cl	H

Table 1a (continuation)

Compound	R	R'	R''
146	2-Br	4-Br	H
147	3-NHSO ₂ CF ₃	4-CH ₃	6-CH ₃
148	3-NHSO ₂ CF ₃	4-CH ₃	5-CH ₃
149	2-F	4-F	H
150	3-CF ₃	H	H
151		H	H
152	2-Cl	6-Cl	H
153	2-Cl	3-Cl	4-Cl
154	2-Cl	4-Cl	5-Cl
155*	3-NO ₂	4-CH ₃	6-CH ₃
156	3-NH ₂	4-CH ₃	6-CH ₃
157	3-CN	H	H
158	2-CN	H	H
159	3-SCH ₃	H	H
160	3-SOCH ₃	H	H
161	3-NO ₂	H	H
162	2-NO ₂	H	H
163	2-CH ₃	4-Br	H
164	2-CN	4-Cl	H
165	3-CF ₃	4-Cl	H
166	3-CF ₃	4-NO ₂	H
167	4-CF ₃	2-NO ₂	H
168	2-CH ₃	4-Cl	H
169	3-NO ₂	4-Cl	H
170	3-OCF ₃	H	H
171	4-OCHF ₂	H	H
172	2-OCHF ₂	H	H
173	4-OCF ₂ CHF ₂	H	H

60

* Compound 155 has a melting point of 127°-129°C.

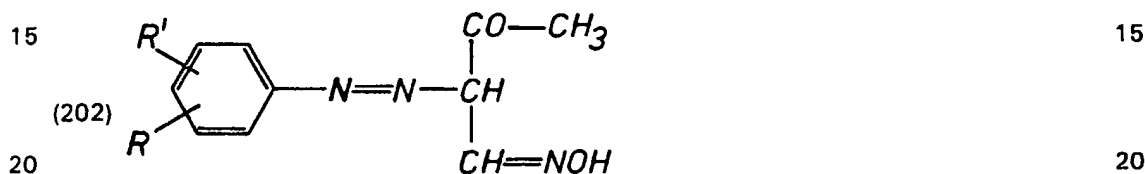
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The other 2-phenyl-2H-1,2,3-triazoles of the formula (1) can also be obtained by using the correspondingly substituted starting compounds of the type of formula (201).

Example 2: 2-Phenylazoacetoacetaldehyde-1-oxime of the formula (201) is prepared as follows:

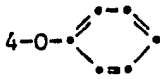

- 5 To a suspension of 190 g of 2-phenylazoacetoacetaldehyde of the formula (301) in 300 ml of ethanol is added a solution of 170 g of sodium acetate trihydrate in 300 ml of water, followed by the addition of a solution of 76.5 g of hydroxylamine hydrochloride in 100 ml of water. The suspension is stirred for 5 hours at 50°C and cooled to 20°C. The precipitate is filtered with suction, washed with water and dried, affording 190 g (92.5% of theory) of 2-phenylazoacetoacetaldehyde-1-oxime of the formula (201) with a melting point of 152°–153°C after crystallisation from toluene. 10

The 2-phenylazoacetoacetaldehyde-1-oximes of the formula

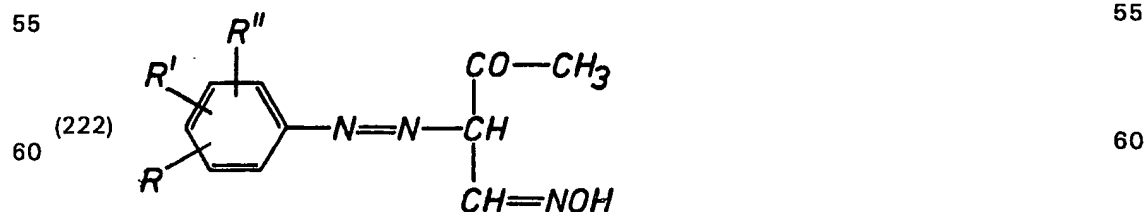


listed in Table 2 can also be obtained by using the correspondingly substituted 2-phenylazoacetoacetaldehydes of the formulae (303)–(321) as starting materials (see Example 3).

Table 2

Compound	R	R'	melting point (°C)
203	4-CN	H	183-185
204	4-CH ₃	H	195-197
205	3-CH ₃	H	167-168
206	2-CH ₃	H	175-176
207	4-Cl	H	196-197
208	3-Cl	H	171-172
209	2-Cl	H	174-175
210	4-OCH ₃	H	163-165
211	3-OCH ₃	H	131-132
212	2-OCH ₃	H	190-192
213	4-COOH	H	243-247
214	4-NO ₂	H	222-224
215		H	129-131
216	4-Cl	2-Cl	197-199
217	4-SO ₂ CH ₃	H	203-204
218	3-SO ₃ Na	H	-
219		H	250-252
220	4-F	H	
221	4-Br	H	

The 2-phenylazoacetaldehyde-1-oximes of the formula




listed in Table 2a as well as the other oximes comprised by formula (6) can be obtained in analogous manner using the correspondingly substituted starting compounds of the type of

formula (301).

Table 2a

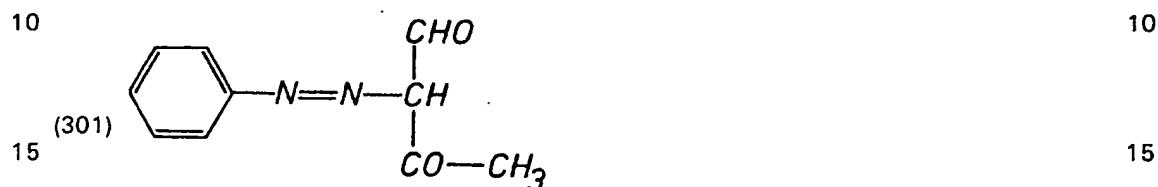
5	Compound	R	R'	R''	5
	223	4-C ₂ H ₅	H	H	
10	224	3-Br	H	H	10
	225	2-F	H	H	
	226	4- I	H	H	
15	227	3- I	H	H	15
	228	2- I	H	H	
	229	4-CF ₃	H	H	
20	230	2-CF ₃	H	H	20
	231	4-i-C ₃ H ₇	H	H	
25	232	4-N(CH ₃) ₂	H	H	25
	233	3-CH ₃	4-Br	H	
	234	3-NH ₂	H	H	
30	235	3-NHSO ₂ CF ₃	H	H	30
	236	3-NO ₂	4-CH ₃	H	
	237	3-NH ₂	4-CH ₃	H	
35	238	3-NHSO ₂ CF ₃	4-CH ₃	H	35
	239	3-Cl	4-CH ₃	H	
	240	3-NH ₂	4-Cl	H	
40	241	3-NHSO ₂ CF ₃	4-Cl	H	40
	242	3-Cl	4-Cl	H	
	243	3-OCH ₃	4-OCH ₃	H	
45	244	3-OCH ₃	5-OCH ₃	H	45

Table 2a (continuation)

Compound	R	R'	R''
245	3-Cl	5-Cl	H
246	2-Br	4-Br	H
247	3-NHSO ₂ CF ₃	4-CH ₃	6-CH ₃
248	3-NHSO ₂ CF ₃	4-CH ₃	5-CH ₃
249	2-F	4-F	H
250	3-CF ₃	H	H
251	4-  -Cl	H	H
252	2-Cl	6-Cl	H
253	2-Cl	3-Cl	4-Cl
254	2-Cl	4-Cl	5-Cl
255	3-NO ₂	4-CH ₃	6-CH ₃
256	3-NH ₂	4-CH ₃	6-CH ₃
257	3-CN	H	H
258	2-CN	H	H
259	3-SCH ₃	H	H
260	3-SOCH ₃	H	H
261	3-NO ₂	H	H
262	2-NO ₂	H	H
263	2-CH ₃	4-Br	H
264	2-CN	4-Cl	H
265	3-CF ₃	4-Cl	H
266	3-CF ₃	4-NO ₂	H
267	4-CF ₃	2-NO ₂	H
268	2-CH ₃	4-Cl	H
269	3-NO ₂	4-Cl	H
270	3-OCF ₃	H	H
271	4-OCHF ₂	H	H
272	2-OCHF ₂	H	H
273	4-OCF ₂ CHF ₂	H	H

Example 3: 2-Phenylazoacetoacetaldehyde of the formula (301) is prepared as follows:

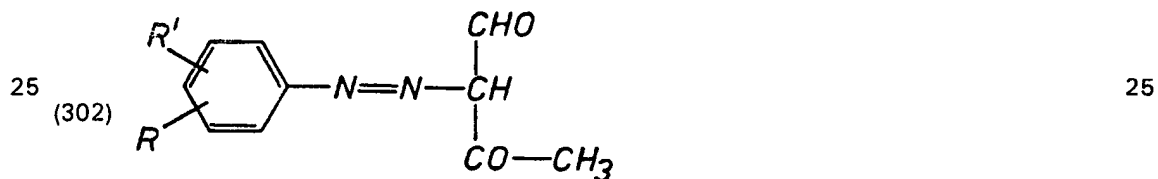
A diazonium salt solution prepared in conventional manner from 1 mole of aniline is stirred into an aqueous solution of 1.1 moles of 1-dimethylaminobut-1-en-3-one at 5°–6°C [cf. D. Leuchs, Chem. Ber. 98, 1335, (1965)]. The pH of the coupling solution is kept at 3.8–4 by adding sodium acetate in portions. Stirring is continued at 12°–15°C until the coupling is complete, and then the yellow coupling product is filtered with suction. The filter cake is washed with water and dried, affording 175 g (92% of theory) of 2-phenylazoacetoacetaldehyde of the formula



in the form of a yellow orange product which melts at 117°–118°C after recrystallisation from ethanol.

20 The 2-phenylazoacetoacetaldehydes of the formula

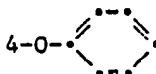

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30 listed in Table 3 are also obtained in analogous manner using the diazonium salt solutions of the correspondingly substituted anilines as starting compounds.

30

Table 3

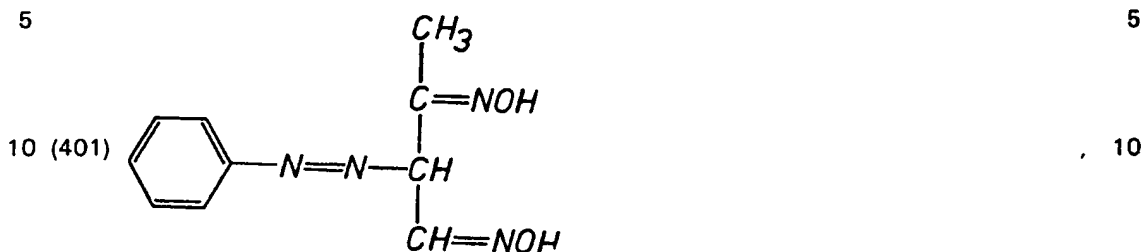
Compound	R	R'	melting point (°C)
303	4-CN	H	156-158
304	4-CH ₃	H	103-105
305	3-CH ₃	H	76-77
306	2-CH ₃	H	91-92
307	4-Cl	H	122-123
308	3-Cl	H	114-115
309	2-Cl	H	117-118
310	4-OCH ₃	H	107-109
311	3-OCH ₃	H	94-96
312	2-OCH ₃	H	119-121
313	4-COOH	H	234-236
314	4-NO ₂	H	177-178
315		H	79-81
316	4-Cl	2-Cl	121-122
317	4-SO ₂ CH ₃	H	167-168
318	3-SO ₃ Na	H	>300
319		H	>300
320	4-F	H	
321	4-Br	H	

2-Phenylazoacetoacetaldehydes which contain in the phenyl ring the same substituents as compounds (223) to (273) (Table 2a) as well as the other 2-phenylazoacetoacetaldehydes comprised by formula (7) are also obtained in analogous manner using the correspondingly substituted anilines and the corresponding compounds of the 1-dimethylaminobut-1-en-3-one type as starting materials.

Example 4:

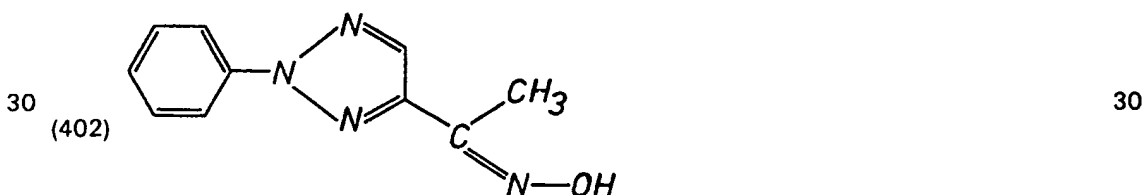
a) 190 g of 2-phenylacetoacetaldehyde of the formula (301) are suspended in 400 ml of pyridine of 15°C and to this suspension are added 146 g of hydroxylamine hydrochloride in portions while keeping the temperature at 15°-20°C by external cooling. The resultant dark solution is then stirred for 16 hours at room temperature. Then 600 ml of water are added and

the reaction mixture is well stirred. The precipitated reaction product is filtered with suction, washed with water and dried, affording 207 g (94% of theory) of the 2-phenylazoacetoacetaldehyde-1,3-dioxime of the formula



which melts at 159°–160°C after recrystallisation from a mixture of equal parts of ethanol and water.

b) 220 g of the 2-phenylazoacetoacetaldehyde-1,3-dioxime of the formula (401) are dissolved in 2000 ml of water which contains 80 g of sodium hydroxide. With stirring, 205 g of acetic anhydride are added dropwise at 10°–15°C over 2 hours while keeping the pH between 11.5 and 12 by the simultaneous dropwise addition of concentrated sodium hydroxide solution. When the reaction is complete, the pH of the suspension is adjusted to 6 with dilute hydrochloric acid and the precipitated reaction product is filtered with suction, washed with water and dried. Yield: 200 g (100% of theory) of 4-acetyl-2-phenyl-2H-1,2,3-triazole-oxime of the formula



in the form of a beige product which melts at 175°–176°C after recrystallisation from chlorobenzene.

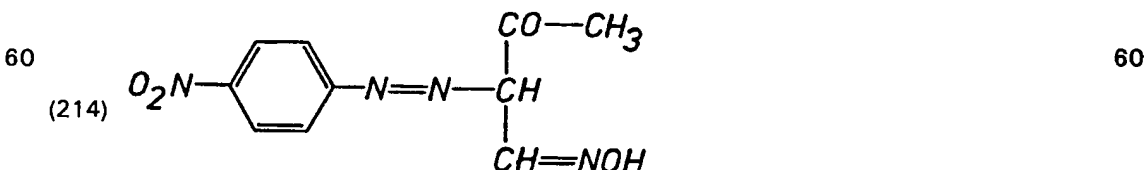
c) With stirring, 20 g of 4-acetyl-2-phenyl-2H-1,2,3-triazoleoxime of the formula (402) and 36.4 g of sodium bisulfite are heated in a mixture of 100 ml of ethanol and 50 ml of water for 24 hours to reflux temperature. After it has cooled, the mixture is diluted with 200 ml of water and adjusted to pH 3 with hydrochloric acid. The precipitated product is filtered with suction, washed with water and dried, affording 17.5 g (93.5% of theory) of 4-acetyl-2-phenyl-2H-1,2,3-triazole of the formula (101) in the form of a beige coloured product which melts at 95°–96°C.

Step c) can also be carried out as follows:

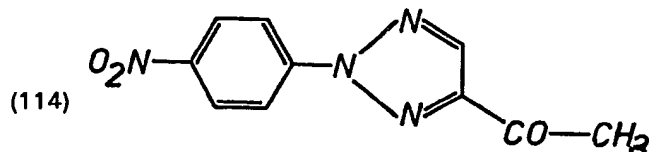
20 g of 4-acetyl-2-phenyl-2H-1,2,3-triazole-oxime of the formula (402) and 4.5 g of paraformaldehyde are heated for 24 hours to reflux temperature in a mixture of 100 ml of water and 10 ml of 30% HCl. After it has cooled, the mixture is diluted with 200 ml of water and the precipitated product is filtered with suction, washed and dried. Yield: 17.9 g (96% of theory) of 4-acetyl-2-phenyl-2H-1,2,3-triazole of the formula (101) in the form of a beige coloured product which melts at 95°–96°C.

The compounds of formulae (103) to (121) listed in Table 1 are also obtained by the method of this Example using the corresponding 2-phenylazoacetoacetaldehydes of the formulae (303) to (321) as starting materials, in which case also the correspondingly substituted intermediates of the formula (401) and (402) type are obtained.

Example 5: 250 g of 2-(4-nitrophenylazo)acetoacetaldehyde-1-oxime of the formula

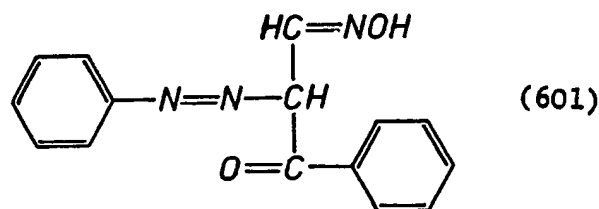


are suspended in 1 litre of water which contains 40 g of sodium hydroxide. The suspension is well stirred for 30 minutes at room temperature, mixed with 1 litre of methylene chloride and the mixture is cooled, with stirring, to 15°C. With efficient stirring, 204 g of acetic anhydride are added dropwise over 1 hour while keeping the pH between 11.5 and 12 by the simultaneous dropwise addition of concentrated sodium hydroxide solution and the temperature at 15°-17°C by external cooling. When the reaction is complete the two-phase mixture is separated and the organic phase is washed with water, dried briefly over magnesium sulfate and concentrated. Yield: 161 g (69.5% of theory) of 4-acetyl-2-(4-nitrophenyl)-2H-1,2,3-triazole of the formula

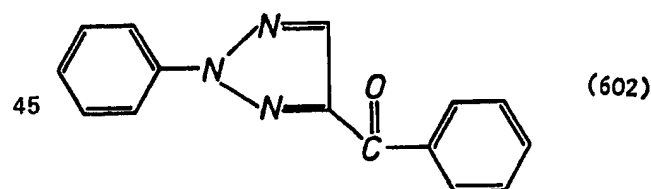


in the form of a brown product which is recrystallised from alcohol to give light brown crystals with a melting point of 123°-125°C.

Example 6: 93.5 g of 3-oxo-3-phenyl-2-phenylazopropionaldehyde-1-oxime of the formula

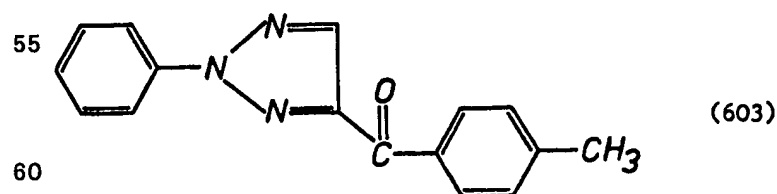


are suspended in 500 ml of water which contains 30 g of sodium hydroxide. The suspension is well stirred for 30 minutes at room temperature, mixed with 300 ml of methylene chloride and the mixture is cooled, with stirring, to 15°C. With efficient stirring, 71.5 g of acetic anhydride are added dropwise over 2 hours while keeping the pH between 11.5 and 12 by the simultaneous dropwise addition of concentrated sodium hydroxide solution and the temperature at 15°-17°C by external cooling. When the reaction is complete the two-phase mixture is separated and the organic phase is washed with water, dried briefly over magnesium sulfate and concentrated. Yield: 81.7 g (94% of theory) of 4-benzoyl-2-phenyl-2H-1,2,3-triazole of the formula



in the form of a yellow orange substance with a boiling point of 165°-170°C/13 Pa and a melting point of 49°-51°C.

The compound of the formula

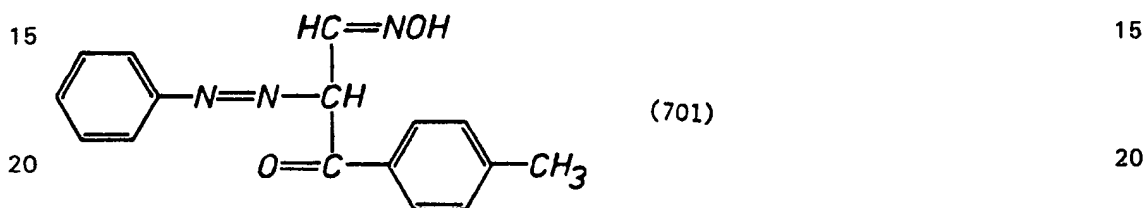


with a boiling point of 177°-182°C/13 Pa and a melting point of 63°-64°C is obtained in analogous manner by the above procedure using 3-oxo-3-(p-methylphenyl)-2-phenylazopropionaldehyde-1-oxime of the formula (701) as starting material.

Example 7: 3-Oxo-3-phenyl-2-phenylazopropionaldehyde-1-oxime of the formula (601) is prepared as follows:

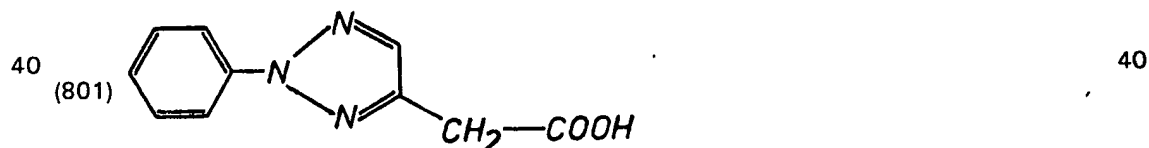
A solution of 85 g of sodium acetate trihydrate in 200 ml of water is added dropwise to a suspension of 126 g of 3-oxo-3-phenyl-2-phenylazopropionaldehyde [known from *Berichte der deutschen Chem. Ges.* 21, 1697 (1888)] in 500 ml of ethanol, followed by the dropwise addition of a solution of 36.5 g of hydroxylamine hydrochloride in 100 ml of water. The suspension is stirred for 20 hours at room temperature and the precipitate is filtered with suction, washed with water and dried. Yield: 124 g (93% of theory) of 3-oxo-3-phenyl-2-phenylazopropionaldehyde-1-oxime of the formula (601) with a melting point of 192°–193°C after crystallisation from ethanol.

3-Oxo-3-(p-methylphenyl)-2-phenylazopropionaldehyde-1-oxime of the formula



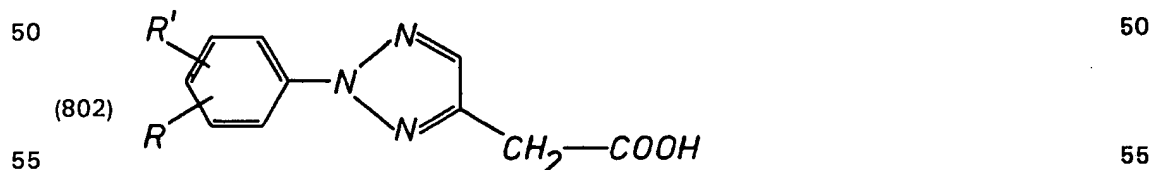
is obtained in analogous manner by the above procedure using 3-oxo-3-(p-methylphenyl)-2-phenylazopropionaldehyde [known from *Berichte der deutschen Chem. Ges.* 59, 108 (1926)] as starting material. Melting point: 206°–207°C after crystallisation from a mixture of ethanol/dimethyl formamide.

Example 8: To a solution of 93.5 g of 4-acetyl-2-phenyl-2H-1,2,3-triazole of the formula (101) in 56.5 g of morpholine are added 17.6 g of powdered sulfur at 70°C and the resultant dark brown melt is stirred for 4 hours at 100°–105°C. Then 250 ml of 17% NaOH are added dropwise and the reaction mixture is kept for a further 4 hours at reflux. After it has cooled to 80°C, the reaction mixture is adjusted to pH 7 with hydrochloric acid, stirred for 30 minutes at this temperature, diluted with water to 1000 ml and clarified by filtration. The clear solution is adjusted to pH 2 with hydrochloric acid and the precipitated beige-coloured product is washed with water and dried. Yield: 90 g (88.5% of theory) of 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acid of the formula



which melts at 109°–110°C after recrystallisation from a mixture of 1 part of toluene and 2 parts of ligroin.

The substituted 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids of the formula



listed in Table 4 are also obtained in analogous manner by using the correspondingly substituted 4-acetyl-2-phenyl-2H-1,2,3-triazoles of the formulae (104) to (113), (116), (117) and (120) as starting materials.

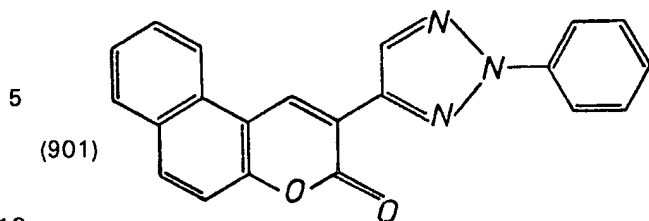
Table 4

Compound	R	R'	melting point (°C)
803	4-CH ₃	H	116-117
804	3-CH ₃	H	86-87
805	2-CH ₃	H	47-48
806	4-Cl	H	151-152
807	3-Cl	H	139-140
808	2-Cl	H	95-96
809	4-OCH ₃	H	140-141
810	3-OCH ₃	H	78-80
811	2-OCH ₃	H	99-101
812	4-COOH	H	264-265
813	4-SO ₂ CH ₃	H	197-198
814	4-Cl	2-Cl	107-109
815	4-F	H	136-140

Other 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids are obtained in analogous manner by using the 2-phenyl-2H-1,2,3-triazoles of the formulae (114), (115), (118), (119), (121) and (123) to (173) as starting materials. The above 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids can be converted by conventional methods into derivatives, for example into salts, esters, thioesters, amides or thioamides.

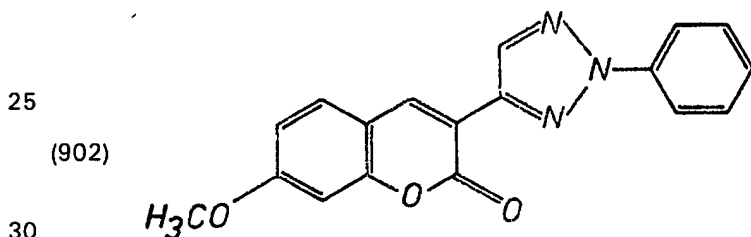
Example 9: As already mentioned, the 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acids and their derivatives (see formula 15) obtained from the 2-phenyl-2H-1,2,3-triazoles of the formula (1) can be used for obtaining fluorescent whitening agents, especially those of the 3-triazol-4'-yl-coumarin series (q.v. US patent specification 3 966 755 and British patent specification 1 412 049). For example, such fluorescent whitening agents may be obtained as follows:

a) 10.3 g of 2-hydroxy-1-naphthaldehyde are added to a mixture of 13.5 g of the sodium salt of 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acid of the formula (801) and 135 ml of acetic anhydride. With stirring, the reaction mixture is heated over 1 hour to the boil and for 5½ hours at reflux. After the reaction mixture has cooled to about 80°C, it is poured into about 1700 ml of cold water and after several hours the precipitated product is filtered with suction, washed and vacuum dried at 60°-70°C. A prepurified product is obtained by recrystallisation from 235 ml of chlorobenzene. Two recrystallisations from chlorobenzene with the aid of fuller's earth yield the compound of the formula



in the form of yellow crystals with a melting point of 238°–238.5°C.

b) 9.9 g of 2-hydroxy-4-methylbenzaldehyde are added to a mixture of 14.6 g of the sodium salt of 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acid of the formula (801) and 130 ml of acetic anhydride. The reaction mixture is heated to the boil over 1 hour and boiled under reflux for 7½ hours. After it has cooled to about 80°C. the reaction mixture is poured into about 1700 ml of water and after hydrolysis of excess acetic anhydride the reaction product is filtered with suction, washed with water until neutral and then stirred with a small amount of alcohol to a paste. The crystals are filtered with suction and again washed with alcohol. Two recrystallisations from chlorobenzene with the aid of fuller's earth yields the compound of the formula



in the form of yellowish crystals with a melting point of 196°–196.5°C.

The following compounds which can be used as fluorescent whitening agents are obtained in accordance with procedure b), but replacing the sodium salt of 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acid of the formula (801) by equivalent amounts of the sodium salts of 2-(m-chlorophenyl)-2H-1,2,3-triazol-4-yl-acetic acid of the formula (807), 2-(p-methylphenyl)-2H-1,2,3-triazol-4-yl-acetic acid of the formula (803) or 2-(p-methyl-m-chlorophenyl)-2H-1,2,3-triazol-4-yl-acetic acid:

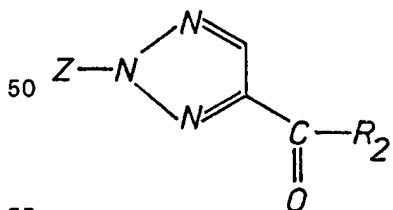
2-(m-chlorophenyl)-4-(7'-methoxycoumarin-3'-yl)-2H-1,2,3-triazole, m.p. 202°–203°C,

2-(p-methylphenyl)-4-(7'-methoxycoumarin-3'-yl)-2H-1,2,3-triazole, m.p. 202.5°–203°C, and

2-(p-methyl-m-chlorophenyl)-4-(7'-methoxycoumarin-3'-yl)-2H-1,2,3-triazole, m.p. 241.5°–242°C.

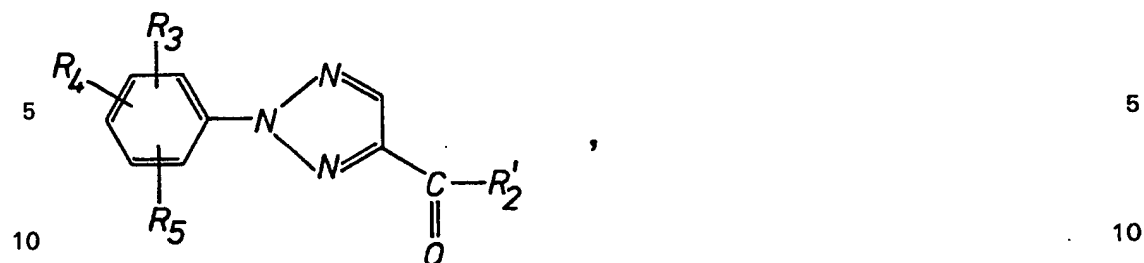
CLAIMS

1. A 2-phenyl-2H-1,2,3-triazole of the formula



wherein R_2 is C_1 – C_6 alkyl, unsubstituted or substituted phenyl or benzyl and Z is unsubstituted or substituted phenyl.

2. A 2-phenyl-2H-1,2,3-triazole according to claim 1 of the formula

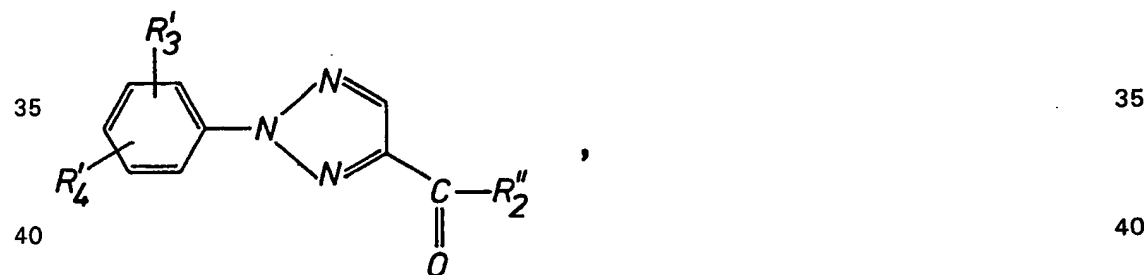


wherein R'_2 is C_1 - C_6 alkyl, unsubstituted phenyl or benzyl, or phenyl or benzyl substituted by one or two members selected from the group consisting of halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_3 - C_4 alkenyl, nitro, cyano, carboxyl or sulfo and their derivatives, C_2 - C_6 carbalkoxy or trifluoromethyl; and R_3 , R_4 and R_5 independently of one another are hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_3 - C_4 alkenyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_2 - C_6 alkoxyalkoxy, or phenyl or phenoxy which is unsubstituted or mono- or polysubstituted by halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_6 carbalkoxy, C_1 - C_4 alkylsulfonyl, cyano, nitro, trifluoromethyl or a group of the formula $-COOY_3$ or $-SO_3Y_3$; or are a group of the formula



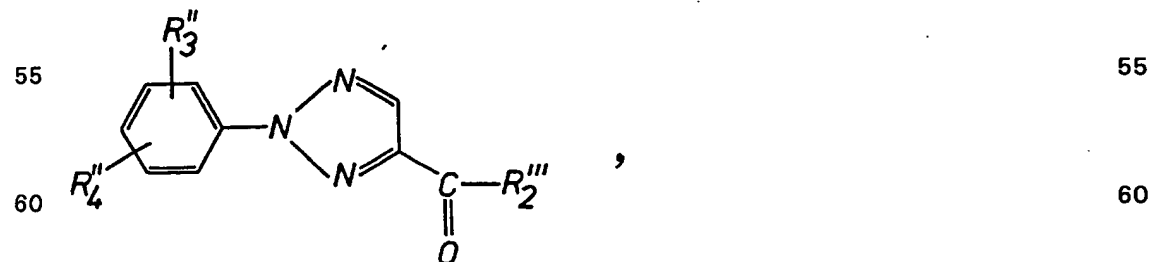
$-NY_1Y_2$, $-SO_3Y_3$, $-COOY_3$, $-S(O)_n(C_1-C_4$ alkyl) or $-S(O)_n(C_1-C_4$ haloalkyl), wherein each of Y_1 and Y_2 independently of the other is hydrogen or C_1 - C_6 alkyl, Y_3 is hydrogen, C_1 - C_4 alkyl or a salt-forming cation and n is 0, 1, or 2.

3. A 2-phenyl-2H-1,2,3-triazole according to claim 2 of the formula



wherein R'_2 is C_1 - C_4 alkyl, benzyl, phenyl or phenyl which is substituted by one or two members selected from the group consisting of chlorine, C_1 - C_4 alkyl, methoxy, nitro, cyano and/or trifluoromethyl, and each of R'_3 and R'_4 independently of the other is hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylsulfonyl, or phenyl or phenoxy which is unsubstituted or substituted by halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, cyano, nitro, trifluoromethyl or a group of the formula $-COOY'_3$ or $-SO_3Y'_3$; or is a group of the formula $-SO_3Y_3$, $-COOY_3$ or $-NY_1Y_2$, wherein Y_1 , Y_2 and Y_3 are as defined in claim 2 and Y'_3 is hydrogen, an alkali metal ion or an ammonium ion.

4. A 2-phenyl-2H-1,2,3-triazole according to claim 3 of the formula



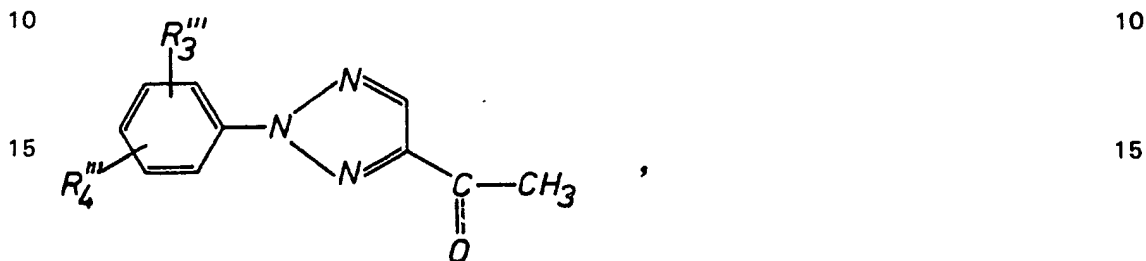
wherein R'_2''' is C_1 - C_4 alkyl, benzyl, phenyl or phenyl which is substituted by one or two substituents selected from the group consisting of chlorine, methoxy and/or methyl, R'_3'' is

hydrogen, halogen, trifluoromethyl, cyano, nitro, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylsulfonyl, or phenyl or phenoxy which is unsubstituted or substituted by chlorine, methyl, methoxy, cyano, nitro, or sulfo or carboxyl or the alkali metal salts or ammonium salts thereof; or is a group of the formula -SO₂Y₃, -COOY₃ or -NY₁Y₂, wherein Y₁, Y₂ and Y₃ are as defined in claim 3; and

5 R₄^{''} is hydrogen, halogen, C₁-C₄alkyl or C₁-C₄alkoxy.

5. A 2-phenyl-2H-1,2,3-triazole according to any one of claims 1 to 4, wherein R₂, R₂['], R₂^{''} or R₂^{'''} are methyl.

6. A 2-phenyl-2H-1,2,3-triazole according to claim 5 of the formula



wherein R₃^{'''} is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄alkoxy, cyano, nitro, or sulfo or carboxyl and the alkali metal salts or ammonium salts thereof, C₁-C₄alkylsulfonyl, phenoxy, phenyl, chlorophenyl, methylphenyl or carboxyphenyl and the alkali metal salts or ammonium salts thereof, and R₄^{'''} is hydrogen, halogen, methyl or methoxy.

25 7. A process for the preparation of a 2-phenyl-2H-1,2,3-triazole of the formula

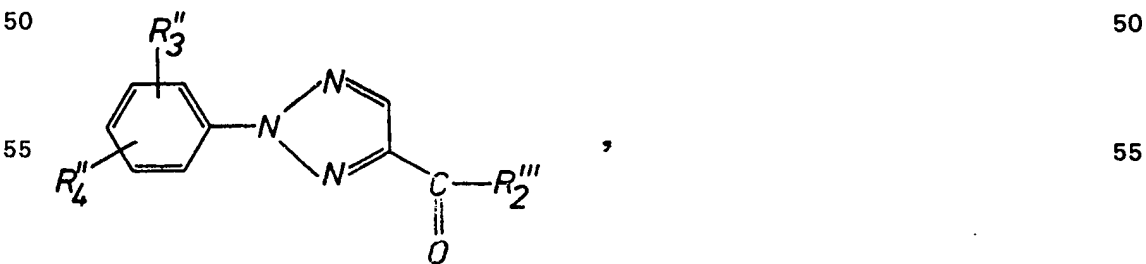


wherein R₂ is C₁-C₆alkyl, unsubstituted or substituted phenyl or benzyl and Z is unsubstituted or substituted phenyl, which process comprises cyclising an oxime of the formula



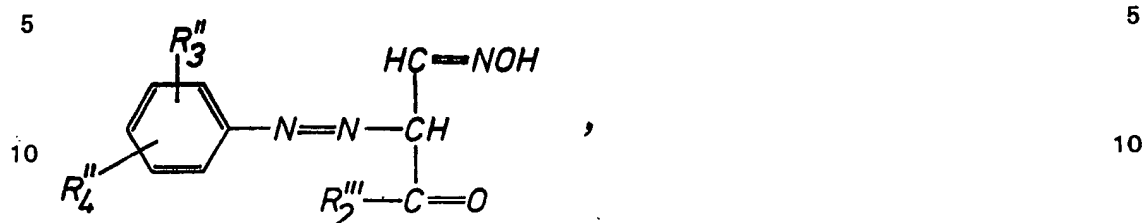
wherein Z and R₂ are as defined above, in the presence of a condensing agent, to the corresponding triazole.

8. A process according to claim 7 for the preparation of a 2-phenyl-2H-1,2,3-triazole of the formula



wherein R₂^{'''} is C₁-C₄alkyl, benzyl, phenyl or phenyl which is substituted by one or two substituents selected from the group consisting of chlorine, methoxy and/or methyl, R₃^{''} is hydrogen, halogen, trifluoromethyl, cyano, nitro, C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylsulfonyl, or phenyl or phenoxy which is unsubstituted or substituted by chlorine, methyl, methoxy, cyano, nitro, or sulfo or carboxyl or the alkali metal salts or ammonium salts thereof; or is a group of

the formula $-\text{SO}_3\text{Y}_3'$, $-\text{COOY}_3'$ or $-\text{NY}_1\text{Y}_2$, wherein Y_1 , Y_2 and Y_3' are as defined in claim 3; and R_4'' is hydrogen, halogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, which process comprises cyclising an oxime of the formula



15 wherein R_2''' , R_3'' and R_4'' are as defined above, in the presence of a condensing agent, to the corresponding triazole. 15

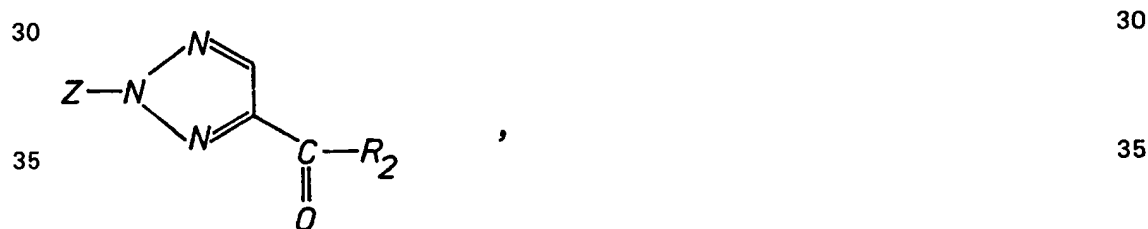
9. A process according to either of claims 7 or 8, wherein the starting material is an oxime, wherein R_2 and R_2''' are methyl.

10. A process according to any one of claims 7 to 9, wherein the condensing agent is an acid anhydride or an acid halide. 20

11. A process according to claim 10 wherein the condensing agent is acetic anhydride, propionic anhydride, acetyl chloride, benzoyl chloride, benzene sulfochloride, toluene sulfochloride, methane sulfochloride, ethane sulfochloride, phosphoroxo chloride or thionyl chloride.

12. A process according to claim 10 or 11, wherein the cyclisation is carried out with acetic anhydride in the presence of water at a pH value between 10 and 13, and the reaction medium may additionally contain a water-miscible organic solvent or, where water-insoluble final products are obtained, a water-immiscible organic solvent. 25

13. A process for the preparation of a 2-phenyl-2H-1,2,3-triazole of the formula



wherein R_2 is C_1 - C_6 alkyl, unsubstituted or substituted phenyl or benzyl and Z is unsubstituted or substituted phenyl, which process comprises reacting a compound of the formula 40



with hydroxylamine or a salt thereof to give a dioxime of the formula



cyclising said dioxime, in the presence of a condensing agent, to give a triazole of the formula



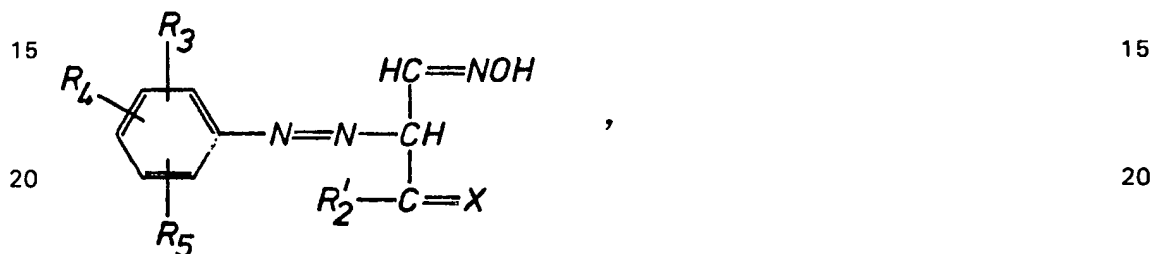
and hydrolysing this latter to the corresponding ketone.

14. An oxime of the formula



10 wherein R_2 is C_1 - C_6 alkyl, unsubstituted or substituted phenyl or benzyl, Z is unsubstituted or substituted phenyl, and X is O or NOH.

15. An oxime according to claim 14 of the formula

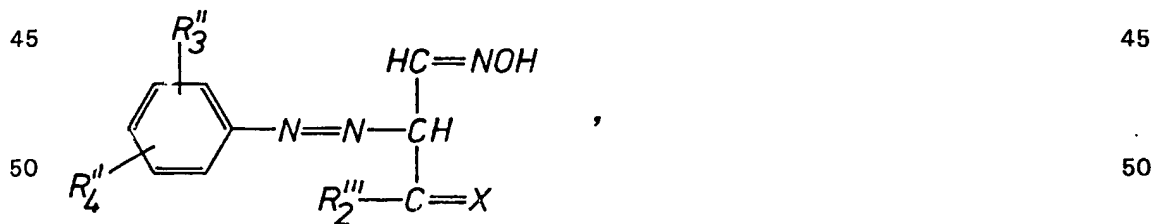


25 wherein X is O or NOH, R_2' is C_1 - C_6 alkyl, unsubstituted phenyl or benzyl or phenyl or benzyl which is substituted by one or two members selected from the group consisting of halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_3 - C_4 alkenyl, nitro, cyano, or carboxyl or sulfo and derivatives thereof, C_2 - C_5 carbalkoxy or trifluoromethyl, and R_3 , R_4 and R_5 independently of one another are hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_3 - C_4 alkenyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_2 - C_6 alkoxyalkoxy, unsubstituted phenyl or phenoxy or phenyl or phenoxy which is mono- or polysubstituted by halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_5 carbalkoxy, C_1 - C_4 alkylsulfonyl, cyano, nitro, trifluoromethyl or a group of the formula $-\text{COOY}_3$ or $-\text{SO}_3\text{Y}_3$; or are a group of the formula



40 $-\text{NY}_1\text{Y}_2$, $-\text{SO}_3\text{Y}_3$, $-\text{COOY}_3$, $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{alkyl})$ or $-\text{S(O)}_n(\text{C}_1-\text{C}_4\text{haloalkyl})$, wherein each of Y_1 and Y_2 independently of the other is hydrogen or C_1 - C_5 alkyl, Y_3 is hydrogen, C_1 - C_5 alkyl or a salt-forming cation, and n is 0, 1 or 2.

16. An oxime according to claim 15 of the formula

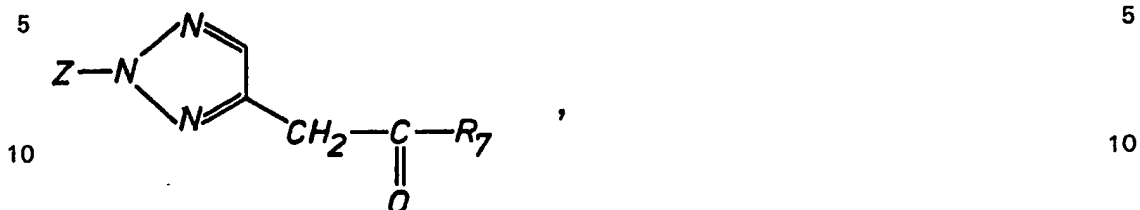


55 wherein X is O or NOH, R_2''' is C_1 - C_6 alkyl, benzyl, phenyl or phenyl substituted by one or two members selected from the group consisting of chlorine, methoxy and/or methyl, R_3'' is hydrogen, halogen, trifluoromethyl, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylsulfonyl, unsubstituted phenyl or phenoxy or phenyl or phenoxy which is substituted by chlorine, methyl, methoxy, cyano, nitro, or sulfo or carboxyl or the alkali metal salts or ammonium salts thereof; or is a group of the formula $-\text{SO}_3\text{Y}_3'$, $-\text{COOY}_3'$ or $-\text{NY}_1\text{Y}_2$, wherein Y_1 , Y_2 and Y_3' are as defined in claim 3; and R_4'' is hydrogen, halogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, with R_3'' preferably being hydrogen, halogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, cyano, nitro, or sulfo or carboxyl and the alkali metal salts or ammonium salts thereof, C_1 - C_4 alkylsulfonyl, phenoxy, phenyl, chlorophenyl, methylphenyl or carboxyphenyl and the alkali metal salts or ammonium salts thereof, and R_4'' preferably being hydrogen, halogen, methyl or methoxy.

65 17. An oxime according to any one of claims 14 to 16 wherein R_2 , R_2' or R_2''' are methyl and

X is O.

18. A process for the preparation of a 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acid of the formula



15 15

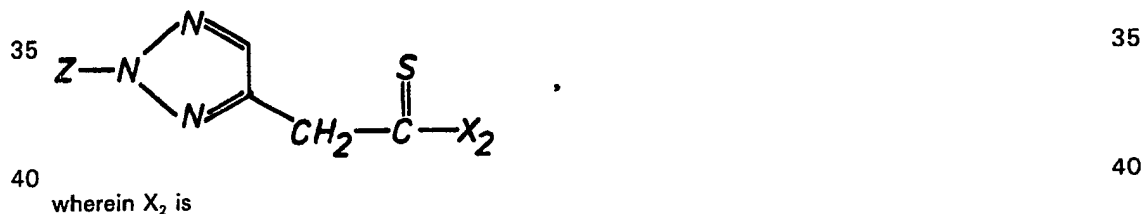
20 20

wherein Z is unsubstituted or substituted phenyl and R₇ is hydroxyl, C₁-C₄alkoxy or a group of the formula -O[⊖]M[⊕] or -NY₄Y₆, wherein each of Y₄ and Y₆ independently of the other is hydrogen or C₁-C₆alkyl, or Y₄ and Y₆ together with the nitrogen atom to which they are attached form a 5- or 6-membered saturated heterocyclic ring which may additionally contain an oxygen, sulfur and/or nitrogen atom as ring members and which may be substituted by one or two C₁-C₄alkyl groups, and M[⊕] is a salt-forming cation, or a derivative thereof, which process



30 30

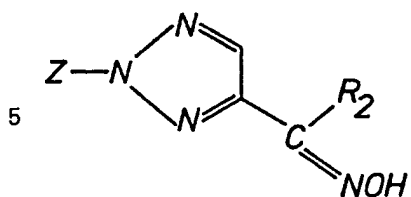
with morpholine, piperidine or dimethylamine and sulfur, to give a 2-phenyl-2H-1,2,3-triazol-4-yl-thioacetamide of the formula



55 55

or -N(CH₃)₂, and hydrolysing this product, without isolating it, to give the corresponding 2-phenyl-2H-1,2,3-triazol-4-yl-acetic acid and, if desired, converting said acid by conventional methods into a salt, an ester or an amide.

19. A 2-phenyl-2H-1,2,3-triazol-4-yl-ketoxime of the formula



10 wherein R_2 is C_1-C_6 alkyl, unsubstituted or substituted phenyl or benzyl and Z is unsubstituted or substituted phenyl. 10

20. A 2-phenyl-2H-1,2,3-triazole according to claim 1 substantially as hereinbefore described with reference to any one of Examples 1, 4, 5 and 6.

21. An oxime according to claim 14 substantially as hereinbefore described with reference 15 to any one of Examples 2, 4, 5 and 7. 15

22. A 2-phenyl-2H-1,2,3-triazol-4-yl-ketoxime according to claim 19 substantially as hereinbefore described with reference to Example 4.

23. A process according to claim 18 substantially as hereinbefore described with reference to Example 8.